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M E M O R A N D U M

STATE WATER CONTROL BOARD

P.O. BOX 11143 RICHMOND, VIRGINIA 23230

SUBJECT: OWRM Guidance Memo No. 91-026
Oil and Grease Analysis Manual

TO: Regional Directors

FROM: Larry G. Lawson, Director
Office of Water Resources Management

DATE: November 18, 1991

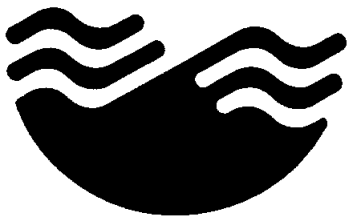
COPIES: Bob Burnley, Technical Services Supervisors, Martin Ferguson, Richard Ayers, Jack Vanderland, Inspector Supervisors, Bill Purcell

Attached is the revised Oil & Grease Manual that will be used in the inspector training (January 22 - 25, 27 - February 1). Inspectors are advised to review the manual for changes to the method. Contact Bill Purcell if additional copies are needed.

Attachment

bp24/sph

OIL & GREASE ANALYSIS



LABORATORY INSPECTION TRAINING MANUAL

OIL AND GREASE

ANALYSIS

REVISED BY:

VIRGINIA WATER CONTROL BOARD
OFFICE OF WATER RESOURCES MANAGEMENT
1991

Contents

1. INTRODUCTION

The wastewater Oil and Grease training manual and the program for which it was developed are designed to provide the information required for an inspector to evaluate the subject parameter. The reader is cautioned to pay particular attention to the safety precautions listed for this analysis.

The manual will provide detailed instruction for preparation of chemicals and equipment, sampling, analysis, calculation, and interpretation of test data for the Oil and Grease analysis.

1.1. Disclaimer

The mention of trade names or commercial products in this manual is for illustrative purposes only and does not constitute any real or implied endorsement or recommendation for use by the Virginia State Water Control Board.

Every effort has been made to provide the reader with the most accurate and detailed information on sampling, analysis, and safety practices for oil and grease testing. However, the Commonwealth of Virginia cannot accept liability for any inaccurate results or injuries resulting from the use of the information supplied. The reader, through the use of this material, accepts full liability for both the accuracy of the reported values and his or her personal safety.

2. LABORATORY SAFETY

2.1. Laboratory Safety Standard

Maintaining safety in the laboratory is really no more difficult than maintaining safety in any other environment. The great majority of accidents in the laboratory are a result of carelessness or inattention with safety guidelines. Inspectors are reminded that new laboratory safety standards became effective January 31, 1991. The standards require that all laboratories:

1. Appoint a chemical hygiene officer

2. Tell each employee about the standard

3. Train each employee about the hazards in their laboratory

4. Formulate a Chemical Hygiene Plan

Any gross hazards encountered during an inspection should be referred to your regional VOSHA Health Supervisor.

The reader is referred to other sources for basic laboratory safety procedures. However, some of the procedures discussed in this manual require special attention to insure the safety of the analyst, such as toxic materials, heat and heating equipment and corrosive chemicals. The following guidelines are provided to address these particular hazards.

2.2. Toxic Materials

Toxic materials can cause injury or death if ingested or absorbed through the skin.

1. Toxic chemicals should always be handled with rubber gloves or pipets with safety bulbs. If the material comes in contact with the skin, it should be washed off immediately.

2. Wash thoroughly before eating, drinking, or smoking.

3. A fume hood should be used to vent potentially toxic gases.

2.3. Heat

The test procedure in this manual requires heating of the test samples. To insure against injuries caused by heat:

1. Use asbestos gloves or tongs to handle hot or potentially hot glassware. Never assume that a beaker or flask is cool.

2. Always wear goggles or face shields when heating or mixing samples and reagents.

2.4. Corrosive Materials

Acids or bases can be corrosive and care should be taken in handling them.

1. NEVER add water to acid, ALWAYS add acid very slowly to water.

NOTE: Acids and bases when mixed with water can generate heat. Care should be taken to protect the analyst from heat burns.

2. If strong acid or base solutions are spilled on your skin or in your eyes, flush with large amounts of water, and seek medical attention immediately.

3. Never put medication or neutralizing chemicals into your eyes unless directed by a doctor.

4. A mild basic solution can be used to neutralize any acid remaining after flushing spills on your skin.

5. A mild acidic solution can be used to neutralize any base remaining after flushing spills on your skin.

Acid and base neutralizing solutions or powders should be available to clean up spills on laboratory bench tops or floors. These types of spills, left unattended, can cause injury to laboratory personnel or damage to clothing long after the spill has occurred.

3. GREASE AND OIL TESTING

The terms grease and oil, as they are applied to wastewater treatment, are not clearly defined. In this determination, absolute quantities of specific substances are not measured. Instead, groups of substances with similar characteristics are isolated through a common solubility in the solvent and a specific boiling point. For this procedure, the parameter is defined by the method.

The materials determined collectively by this procedure include relatively non-volatile hydrocarbons, soaps, waxes, fats, oils, and any other materials that are extracted by the solvent and are not volatilized during the test.

Conversely there are materials which are either totally or partially lost during the solvent removal operation. Petroleum hydrocarbons such as gasoline through #2 fuel oils will not be quantitatively recovered. For samples containing these types of products other methodologies would be appropriate. An inspector should be alert to facilities which have inappropriate monitoring requirements. Some crude oils and heavy fuel oils will contain residues which are not soluble in trichlorotrifluoroethane (Freon)

Other materials are extracted from an acidified sample such as sulphur compounds, certain organic dyes, and chlorophyll, which give a positive bias to the procedure.

3.1. Effects of Grease and Oil in Wastewater Treatment

A variety of undesirable effects are produced by greases and oils in wastewater treatment. Most greases and oils are insoluble in water and float on the surface producing slicks or scum which are odorous and difficult to dispose of. In secondary treatment processes, greases and oils coat organic particles in the wastewater inhibiting oxygen transfer and biodegradation by microorganisms.

Greases and oils can also adhere to the surface of equipment reducing the operating efficiency of such things as pumps, pipelines, screens and filters.

Lastly, the presence of greases and oils on walkways and ladders is a safety hazard in the treatment plant.

3.2. EPA Approved Method

The EPA approved method for this parameter is listed in both in the 1979 edition of Methods of Chemical Analysis of Water and Wastes (413.1) and the 17th Edition of Standard Methods (5520 B). The method uses an extraction with trichlorotrifluoroethane (Freon) and a gravimetric finish. After extraction, the Freon solvent is evaporated (or distilled) and the residue of grease and oil is weighed.

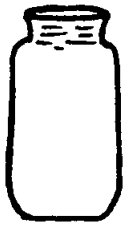
Because the United States is a party to the Montreal Protocol on substances that deplete the ozone layer, EPA is looking for an alternative extraction solvent to Freon. EPA has tentatively identified an 80:20 mixture of n-hexane and methyl tertiary butyl ether (MBTE) as the alternative solvent. Preliminary tests show that the solvent mixture gives similar results to Freon. Inspectors should alert laboratory staff of the impending procedural change to avoid having to dispose of a large quantity of Freon. The proposed solvent is also flammable and potentially explosive.

3.3. Sampling and Preservation

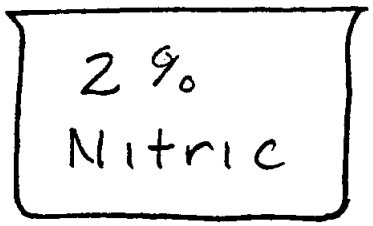
Grease and oil testing must be performed using grab samples. If a profile of the grease and oil concentration in the waste stream is desired, separate grab samples, collected at various times, can be analyzed and the results averaged. Samples cannot be split for duplicate analysis. If duplicates are desired co-located grab samples must be collected and analyzed separately.

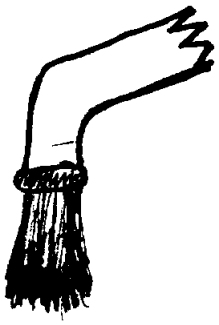
The procedures on the succeeding pages should be followed when sampling for grease and oil in wastewater.

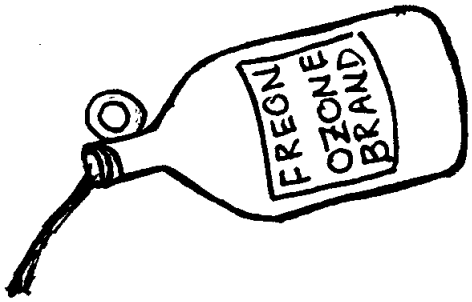
1. Collect samples in **wide-mouth** glass containers which have previously been rinsed with Freon and air-dried. Canning jars may be used for oil & grease sample collection but must be clean and rinsed with solvent. Jars purchased from suppliers of sample containers that are certified to be cleaned to EPA specifications, or that have been muffled after cleaning, do not need to be Freon rinsed. All contact between the sample and rubber or plastic (other than TFE) must be avoided. Sample container lids must be lined with aluminum foil or TFE.



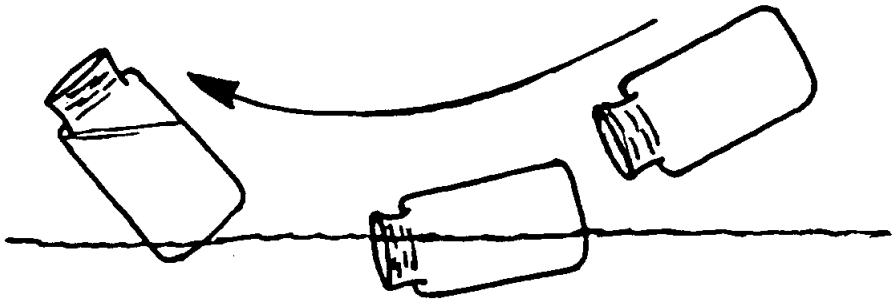
2. If detergents are used to clean glassware it is critical to rinse well with tap and deionized water followed by a solvent rinse and then be allowed to air dry, because of the ability of Freon to extract detergents. A soak in 2% nitric acid followed by rinses in tap water, deionized or distilled water and solvent is the preferred method of cleaning for all but the dirtiest glassware. A method blank should be run periodically to check cleaning procedures.



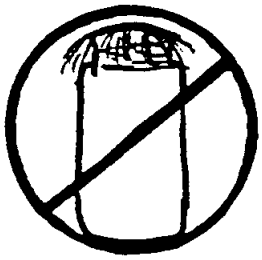




3. Collect samples using a dipping motion along the water surface.

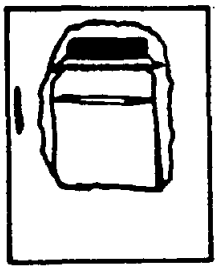


4. Do not fill the sample bottle to overflowing.



5. If analysis is delayed for more than a few hours, the sample is acidified with 5 ml of 1:1 HCL or H_2SO_4.

6. Cap the sample container with aluminum foil or a TFE lined lid and store at 4° C. Do not exceed the recommended holding time of 28 days.



3.4. Equipment

125 ml boiling flasks
2000 mL separatory funnel with **TFE (Teflon)** stopcock
Water bath capable of maintaining 70° C
Analytical balance weighing to 0.1 mg
Filter paper, Whatman No. 40 or equivalent
Distilling head (for solvent recovery)
Vacuum pump or vacuum source
Residue free gloves
Laboratory tissues

3.5. Reagents

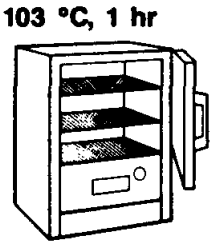
Trichlorotrifluoroethane (Freon), boiling point 47° C
Sodium sulfate, anhydrous crystals

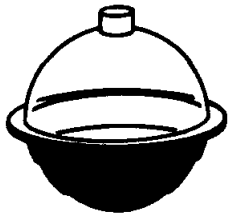
3.6. Special Handling of Freon

The Freon solvent should leave no measurable residue on evaporation. A solvent blank should be run on each new bottle of Freon. If recovered solvent is being used a blank must be run with each series of samples.

3.7. Preparation

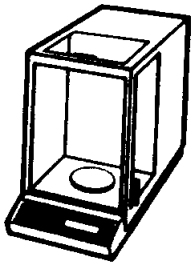
1. Dry the boiling flask at 103° C for one hour, then place the flask in a desiccator for at least 30 minutes or until ready for use. Handle the flask with residue free gloves or "Kimwipes" to avoid adding fingerprints.





NOTE: Follow previously described cleaning procedures for the boiling flasks.

2. Weigh the boiling flask on an analytical balance. Record weight to 0.1 mg.

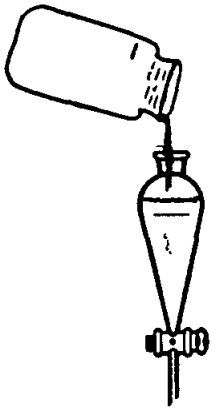


3.8. Extraction

1. Mark the sample bottle at the meniscus for later determination of sample volume.

2. Check the pH of the sample by touching pH sensitive paper to the cap to insure the sample is pH is 2 or lower. If not done previously, acidify the sample to pH 2 with 1:1 sulfuric or hydrochloric acid.

3. Transfer the sample from the marked sample container to a 2000 mL separatory funnel.



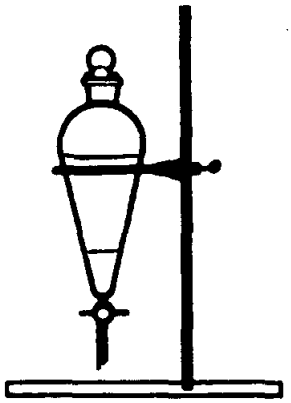
4. Rinse the sample container with 30 mL Freon and transfer the solvent to the separatory funnel. When rinsing the sample container make sure that the cap is replaced so that any oil and grease residue adhering can be extracted.

5. Stopper the funnel and invert. Release the pressure by opening the stopcock.

6. Mix gently for five seconds and again release the pressure. Repeat mixing and pressure release.

7. Shake the funnel vigorously for two minutes and again release the pressure. For samples where it is suspected that vigorous agitation would form a stable emulsion, gently shake the separatory funnel for 5 to 10 minutes.

8. Reinvert the funnel and allow the Freon and water layers to separate.

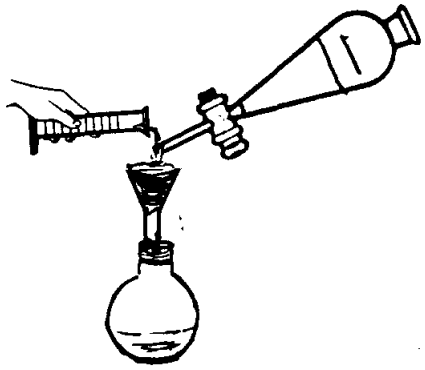


9. Remove the separatory funnel stopper and drain the Freon layer into a previously weighed boiling flask.

10. If the Freon layer is cloudy or contains an emulsion layer, filter it through filter paper containing one gram of sodium sulfate.

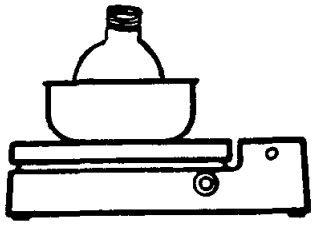
11. Repeat Steps 4-10 twice using 30 mL of Freon each time and combine the extracts in the boiling flask.

12. Rinse the tip of the separatory funnel and the filter, if used, with 10-20 mL of Freon and combine with the extracts in the boiling flask.

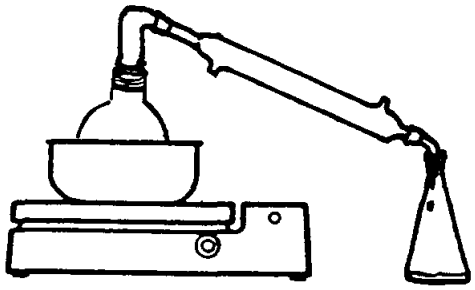


3.9. Evaporation and Weighing

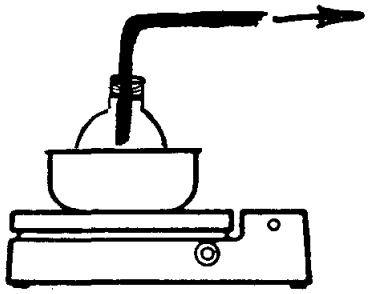
1. Place the boiling flask on a 70° C water bath located in a well ventilated area and evaporate the Freon from the flask.



2. It is recommended that the Freon be distilled from the flask and the distillate collected for reuse. Inspectors should stress this issue and point out the environmental and economic benefits.

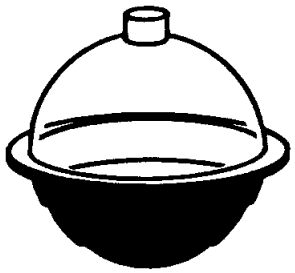


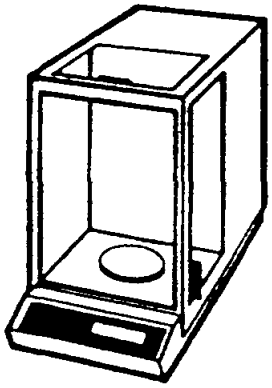
3. Evacuate the remaining Freon vapor with an applied vacuum for the final 15 seconds of the evaporation.



4. Remove excess moisture and fingerprints from the flask using a clean cotton cloth or lint-free laboratory tissue.

5. Cool the flask in a desiccator for 30 minutes, then weigh the flask and residue on an analytical balance.





6. Determine the volume of sample by filling the sample container to the liquid level mark with water and measure this volume by pouring it into a graduated cylinder.

3.10. Calculation

$$\text{Grease and Oil, mg/L} = \frac{(R - B) \times 1000}{\text{mL Sample}}$$

R = residue, gross weight of the extraction flask minus the tare weight, in milligrams

B = blank determination, residue of equivalent volume of extraction solvent, in milligrams

3.11. Interferences

Freon does not selectively dissolve grease and oil and, as such, other organic substances present in the sample may appear as grease and oil in the final result.

The evaporation or distillation step to remove the Freon solvent will result in the loss by volatilization of short chain hydrocarbons, simple aromatics and significant amounts of petroleum distillates from gasoline to No. 2 fuel oil. Heavier residuals of petroleum may also contain large amounts of Freon insoluble materials.

Certain wastewaters, such as those from poultry processing operations, may form stable emulsions. Many of these industries have received a variance to perform a Soxhlet extraction. See section 4.0 for additional discussion of the Soxhlet extraction.

3.12. Example Oil and Grease Determination

A sample for oil and grease analysis is collected from the effluent of a wastewater treatment plant. The initial weight of the boiling flask used in the determination is 37.5942 g. At the end of the test, the weight of the flask and oil and grease residue is 37.5975 g. The volume of sample determined for the test is 965 ml. The weight of the blank is 0.0003 g

The mg/l oil and grease is calculated as follows:

Wt. of residue and flask = 37.5975
Wt. of flask = 37.5942
Wt. of residue = .0033

Multiply the Wt. of residue by 1000 to convert to mg.

$0.0033 \times 1000 = 3.3$ mg

Multiply the Wt. of blank by 1000 to convert to mg.

$0.0003 \times 1000 = 0.3$ mg

$$\text{mg/l oil and grease} = \frac{\text{mg residue} \times 1000}{\text{ml sample}}$$

$$= \frac{(3.3 - 0.3) \times 1000}{965}$$

$$= 3.1 \text{ mg/l}$$

4. SOXHLET EXTRACTION

As discussed earlier permittees wishing to use the Soxhlet extraction for oil & grease determination must obtain a variance for its use in VPDES monitoring. Industries having concentrations of fat and grease in their wastewater, such as meat and poultry processors, are likely candidates for this method. Since the extraction takes place at an elevated temperature there will be no recovery of volatile Freon extractables. Sample collection and preservation is the same as for the gravimetric-partition procedure.

4.1. Equipment

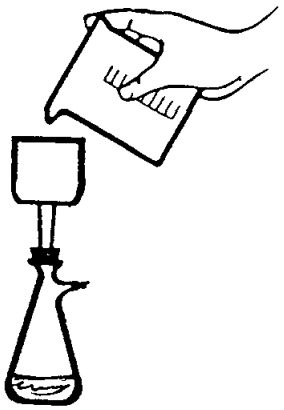
125 ml boiling flasks
Soxhlet extraction apparatus
12 cm Buchner funnel
Electric heating mantle
Paper extraction thimble
11 cm diameter filter paper (Whatman 40 or equivalent)
11 cm diameter muslin cloth disks
Vacuum source
Sidearm vacuum flask
103° C hot air oven

4.2. Reagents

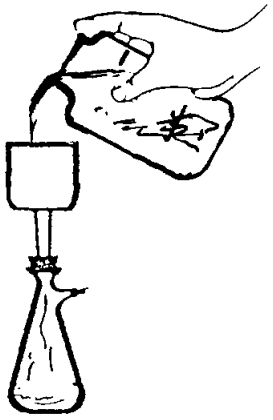
1 + 1 HCL
Trichlorotrifluoroethane (Freon)
10 g/l diatomaceous-silica filter aid suspension (Hyflo Super-Cel, Johns Manville Corp., or equivalent)

4.3. Extraction

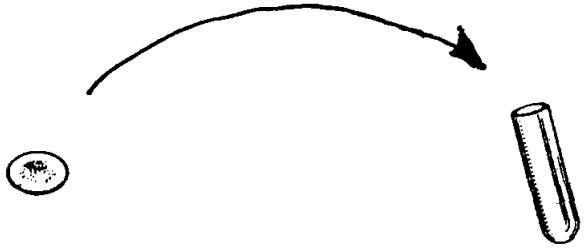
1. Prepare filter by placing filter paper over muslin cloth disk. Wet the paper and cloth with distilled water and seat the filter paper. Place Buchner funnel in a sidearm flask and pour 100 ml of filter aid through the filter while under vacuum. Apply vacuum until no more water passes through the filter.



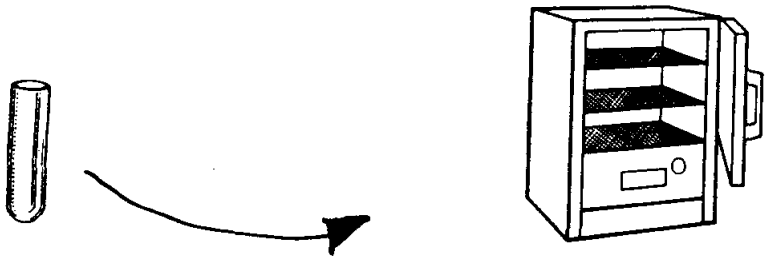
2. Filter acidified sample until no more water passes through filter. Remove filter paper from funnel with forceps and place on a watch glass. Take care to remove all filter paper adhering to the edges of muslin cloth.



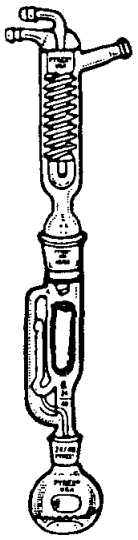
3. With a piece of solvent wetted filter paper carefully wipe the inside of the Buchner funnel and sample container to remove any grease residue. Add pieces of filter paper to filter paper on watch glass. Roll the filter paper containing the sample and place it in a paper extraction thimble. Wipe the watch glass with a piece of solvent wetted filter paper and add the filter paper to the extraction thimble.



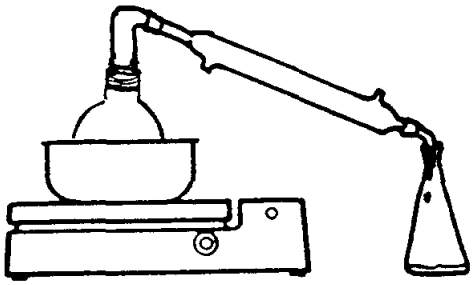
4. Place extraction thimble in a 103^{o} C hot air oven and dry for 30 minutes



5. Fill thimble with small glass beads or glass wool and place thimble in a Soxhlet extraction device. Secure a tared 125 ml extraction flask containing approximately 100 ml of solvent, to the Soxhlet apparatus. Extract oil and grease by refluxing the solvent at a rate of 20 cycles/hour for 4 hours.



6. Distill solvent in a 70° C water bath and proceed as in the partition-gravimetric method. Calculate oil and grease content as described in the gravimetric-partition method.



GRAVIMETRIC ANALYSIS

BENCH SHEET

PARAMETER: _____ ANALYST: _____

DATE ANALYZED: _____

METHOD: _____

REFERENCE:

SAMPLE IDENT.

SAMPLE DATE

mL SAMPLE

VESSEL NO.

WT. TARE + RES.

WT. TARE

WT. RESIDUE

mg/L

SAMPLE IDENT.

SAMPLE DATE

mL SAMPLE

VESSEL NO.

WT. TARE + RES.

WT. TARE

WT. RESIDUE

mg/L

EXAMPLE CALCULATION:

COMMENTS:

APPENDIX A

ANALYTICAL BALANCES

ANALYTICAL BALANCES

In the oil and grease procedure, the most important piece of equipment relative to the accuracy of the test results is the analytical balance used for the determination. Any model of balance will be suitable for use in the test, as long as it will weigh to at least 0.1 mg. In most wastewater laboratories the most common type of analytical balance is the "single pan" variety.

"Single pan" balances feature mechanical lifting and substitution of the weights, mechanical zeroing of the empty balance and digital weight readouts. Some of the precautions to be observed to maintain the accuracy and prolong the life of the balance are:

1. Locate the balance away from routine laboratory traffic, direct sunlight, drafts, excessive humidity or sudden temperature changes.

2. Mount the balance on a heavy, shock proof table with adequate working surface.

3. Check the balance level at least daily and adjust as needed.

4. Disengage the balance weights when the balance is not in use.

5. To avoid spilling corrosive chemicals on the balance pan or in the pan enclosure use weighing boats, weighing papers or some similar item.

6. Check the sensitivity and accuracy of the balance at least semi-annually with a set of standard balance weights.

7. Have the balance serviced by a qualified specialist at least annually.

8. Follow the manufacturers instructions at all times.

It is important to read and follow the operating instructions supplied with your balance. If you do not have the operating instructions for your balance, the following steps should provide a general outline of the weighing procedure for a "single pan" balance.

1. Level and zero the balance before use.

2. If the procedure calls for the determination of weight gained, such as in the oil and grease test, place an empty container on the balance pan and close the doors to the pan enclosure.

3. If the balance is equipped with a preweighing feature, turn the pan release knob to that position.

4. Determine the approximate gram weight of the empty container and dial in the weight on the balance.

5. Turn the pan release knob to the full release position.

6. Allow the container and pan to stabilize, then dial in the appropriate milligram weights to obtain the tare weight of the empty container.

7. Record the tare weight of the empty container on the data sheet for the test.

8. Turn the pan release knob to the full arrest position, return all of the weight dials to zero and remove the empty container from the balance pan.

NOTE: Never remove an object from the balance pan or dial on or off gram weights if the balance is in the full release position.

9. After the test procedure to produce a residue has been completed, repeat these steps to obtain the weight of the container and residue.

10. Record the final weight of the container and residue on the data sheet for the test and complete any calculations needed to obtain the final result.

APPENDIX B

REFERENCES

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